Conventional techniques fail to estimate high-overtone diatomic transition probabilities

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Calculating probabilities of high-overtone ro-vibrational transitions is particularly challenging. While the experimental intensities available for low Δn (change in the vibrational quantum number) values are well reproduced by a variety of methods but the most results greatly diverge in predicting the probabilities of unobserved higher-overtone transitions. The failure often appears as flattening (saturation) of the calculated transition dipole moments δon starting at some Δn which depends on both the molecule and the method used. For example, in carbon monoxide, Δn = 10 if the calculations are performed with double precision arithmetic⁴, and Δn = 7 if a cubic spline-interpolated dipole-moment function (DMF) is used⁵. The flattening is revealed when the calculated probabilities are compared with the theoretical NIDL⁶ (Normal Intensity Distribution Law) predictions, as demonstrated in Fig. 1.

![Graph showing the comparison of various DMFs](image)

Fig. 1: Square of the CO 0→n (n=1-40) transition dipoles vs square root of upper-state energy v₀ in units of vibrational quantum hv₀ calculated with quadruple precision. Crosses, analytical (polynomial) DMF; triangles, non-analytical (spline-interpolated ab initio) DMF; straight line, NIDL predicted by an analytical theory.

References